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(54) Title of the Invention: LIGHT-EMITTING BALL

(21) Application No. S59-79608 (22) Filing Date: April 20, 1984

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Patent Specification

1. Title of the Invention: Light-Emitting Ball

2. Claims:

- (1) A light-emitting ball comprising a light-emitting body filled with a chemical light-emitting composition composed of two or more reagents which, when mixed, generate light, wherein said light-emitting body is inserted into a ball, said lightemitting body being filled with the aforementioned chemical reagents so that the aforementioned chemical reagents are mixed when an external force is applied to said ball at the initial moment of use.
- (2) The light-emitting ball of Claim 1, wherein the chemical light-emitting composition consists of the components (a), (b), (c), and (d) given below:
 - (a) a compound represented by the following general formula:

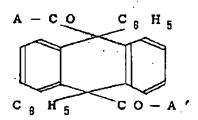
$$A - CO - CO - A'$$

[where A and A' may be the same or different and designate: (i) -OR (where R is an optionally substituted alkyl group, aryl group, or a heterocyclic group such as a pyridyl or a phthalimide group); (ii) – OCOR₁ (where R1 is an optionally

 R_2 substituted alkyl group or an aryl group); (iii) -N < (wherein at least one R_3

of R_2 and R_3 is an electrically polar substituent that provides a signal value of about +0.7, while the other substituents are a hydrogen atom, aryl group, or a heterocyclic ring that is formed by R_2 and T_3 together with nitrogen and that contains an oxygen or a ketone group)];

- (b) a hydroxyperoxide or a compound that produces hydroxyperoxide;
- (c) an optional component, such as a diluent, water, and an acidic or basic catalyst;
- (d) an organic luminescent agent [this agent can be omitted if component (a) possesses self-luminescent properties or if a reaction product obtained by mixing components (a), (b), and (c) possesses luminescence].
- (3) The light-emitting ball of Claim 1, wherein said chemical light-emitting composition consists of the components (a), (b), (c), and (d) given below:
 - (a) a compound of the following general formula:



[where A and A' may be the same or different and are represented by any of the following groups (i), (ii), or (iii): (i) -OR (where R is an optionally substituted alkyl group, aryl group, or a heterocyclic group such as a pyridyl or a phthalimide group); (ii) – OCOR₁ (where R1 is an optionally substituted alkyl group or an

aryl group); (iii)
$$-N < (wherein at least one of R_2 and R_3 is such an $R_3$$$

electrically polar substituent that provides a signal value of about +0.7, while the other substituents are a hydrogen atom, aryl group, or a heterocyclic ring that is formed by R_2 and T_3 together with nitrogen and that contains an oxygen or a ketone group)];

- (b) a hydroxyperoxide or a compound that produces hydroxyperoxide;
- (c) an optional component, such as a diluent, water, and an acidic or basic catalyst;
 - (d) an organic luminescent agent [this agent can be omitted if component (a)

possesses self-luminescent properties or if a reaction product obtained by mixing components (a), (b), and (c) possesses luminescence].

- (4) The light-emitting ball of Claim 1, wherein said chemical light-emitting composition consists of the components (a) and (b) given below:
 - (a) a compound of the following general formula:

(where X is an electrically polar substituent selected from the group consisting of chlorine, bromine, a nitro group, or a trifluoromethyl group; R_4 is a carboalkoxy group; R_5 is selected from a hydrogen atom, linear-chain alkyl group, branch-chain alkyl group, or an alkoxyalkyl group; "m", "n", and "q" constitute a set of integers that provides the sum total of the Hammett's sigma values of substituents X, R_4 , and R_5 for respective phenyl groups at least in the range of 1.4 to 2.7; "n" is 0, 1, or a number greater than 1; and "q" is 0, 1, 2, or 3); and (b) at least one of the following: a luminescent agent, hydrogen peroxide, or a diluent.

3. Detailed Description of the Invention [Field of the Invention]

The present invention relates to a light-emitting ball, in particular to a light-emitting ball that, due to the presence of a chemical light-emitting composition, emits light during use.

[Background of the Invention]

With a great deal of attention paid in the recent years to public heath and to development of leisure-time facilities, outdoor and indoor sports also became high on the agenda. People who are busy during the daytime, such as students, companies' employees, as well as just physically active people often find time for sports only in the evenings, mostly on artificially illuminated sport grounds and in gymnasia where many sports such as softball, football, gateball, tennis, volleyball, and, recently, golf are games that involve the use of balls.

However, even though the night-time sport facilities are illuminated, the ball often gets into poorly illuminated areas where it is not clearly visible. Therefore, it

becomes necessary to interrupt the game in order to look for the ball, and this violates the game. Under certain circumstances, invisibility of the ball may lead to an accident or injury.

[Object of the Invention]

It is an object of the present invention to solve the above problems and to provide a light-emitting ball that is clearly visible even under poorly illuminated conditions.

[Description of the Invention]

For accomplishing the above object, the present invention provides a light-emitting ball that emits light when an external force is applied to it during use. More specifically, the invention provides a light-emitting ball comprising a light-emitting body filled with a chemical light-emitting composition having two or more reagents which, when mixed, generate light, wherein said light-emitting body is filled with the aforementioned chemical reagents and is inserted into the ball so that when an external force is applied to said body at the initial period of use, the aforementioned chemical reagents are mixed.

The invention will be further described in more detail with reference to the accompanying drawings.

A light-emitting body that forms the light-emitting ball of the present invention is filled with a chemical light-emitting composition that contains two or more reagents which emit light when mixed. The aforementioned reagents fill the light-emitting body so that when the ball is not in use, the reagents are separated but when an external force is applied to the ball at the initial moment of use, the reagents are mixed.

The following chemical light-emitting compositions I, II, and III that emit light during mixing can be used:

- I. A chemical light-emitting composition that consists of the components (a), (b), (c), and (d) given below:
 - (a) a compound represented by the following general formula:

$$A - CO - CO - A'$$

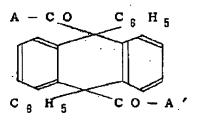
[where A and A' may be the same or different and designate: (i) -OR (where R is an optionally substituted alkyl group, aryl group, or a heterocyclic group such as a pyridyl or a phthalimide group); (ii) – OCOR₁ (where R1 is an optionally

substituted alkyl group or an aryl group); (iii) -N < (wherein at least one R_3

of R₂ and R₃ is an electrically polar substituent that provides a signal value of

about +0.7, while the other substituents are a hydrogen atom, aryl group, or a heterocyclic ring that is formed by R₂ and T₃ together with nitrogen and that contains an oxygen or a ketone group)] (specific examples of the aforementioned component are the following: bistriphenyl acetic acid and oxalic acid anhydride, dilauric acid and oxalic acid anhydride, bis-4-methoxy benzoic acid and oxalic acid anhydride, etc.);

- (b) a hydroxyperoxide or a compound that produces hydroxyperoxide (specific examples of this component are the following: hydrogen peroxide, perbenzoic acid, benzoyl peroxide, peroxylauric acid, di-t-butylperoxide, t-butylhydroperoxide, etc.);
- (c) an optional component, such as a diluent, water, and an acidic or basic catalyst (specific examples of this component are the following: substituted antracene, or a similar fluorescent agent; an organic solvent or a similar diluent, KOH, HCI, or a similar catalyst);
- (d) an organic fluorescent agent [this agent can be omitted if component (a) possesses self-luminescent properties or if a reaction product obtained by mixing components (a), (b), and (c) possesses luminescence].
- II. A chemical light-emitting composition that consists of the components (a) through (d) given below:
 - (a) a compound of the following general formula:



[where A and A' may be the same or different and are represented by any of the following groups (i), (ii), or (iii): (i) -OR (where R is an optionally substituted alkyl group, aryl group, or a heterocyclic group such as a pyridyl or a phthalimide group); (ii) – OCOR₁ (where R1 is an optionally substituted alkyl group or an

aryl group); (iii)
$$-N <$$
 (wherein at least one of R_2 and R_3 is such an R_3

electrically polar substituent that provides a signal value of about +0.7, while the other substituents are a hydrogen atom, aryl group, or a heterocyclic ring that is formed by R₂ and T₃ together with nitrogen and that contains an oxygen or a ketone group)];

- (b) a hydroxyperoxide or a compound that produces hydroxyperoxide;
- (c) an optional component, such as a diluent, water, and an acidic or basic catalyst;

- (d) an organic fluorescent agent [this agent can be omitted if component (a) possesses self-luminescent properties or if a reaction product obtained by mixing components (a), (b), and (c) possesses luminescence].
- III. A chemical light-emitting composition that consists of the components (a) and (b) given below:
 - (a) a compound of the following general formula:

(where X is an electrically polar substituent selected from the group consisting of chlorine, bromine, a nitro group, or a trifluoromethyl group; R_4 is a carboalkoxy group; R_5 is selected from a hydrogen atom, linear-chain alkyl group, branch-chain alkyl group, or an alkoxyalkyl group; "m", "n", and "q" constitute a set of integers that provides the sum total of the Hammett's sigma values of substituents X, R_4 , and R_5 for respective phenyl groups at least in the range of 1.4 to 2.7; "n" is 0, 1, or a number greater than 1; and "q" is 0, 1, 2, or 3) [the following are specific examples of this component: 2,4,5-trichloro-6-carboalkopxyphenyl] oxalate, bis (2,4,5-trichloro-carbobutoxyphenyl) oxalate, bis (2,4,5-trichloro-6-carbopentoxyphenyl) oxalate, or similar bis (phenyl) oxalate ester derivatives];

(b) at least one of the following: a luminescent agent, hydrogen peroxide, or a diluent [specific examples of this component are the following: 9,10-bis (phenylethynyl) antracene, 1-methoxy-9,10 bis (phenylethynyl) antracene, 9,10-diphenyl antracene, perylene, or other fluorescence agents; hydrogen peroxide, tertiary alcohol, tertiary alcohol phthalate esters, or similar solvents].

The above-mentioned chemical light-emitting compositions I, II, and III can emit light when the following components are mixed: (a) and (b); (a), (b), and (c); and (a), (b), (c), and (d).

In accordance with the invention, the aforementioned chemical reagents are loaded into the ball in a premixed state.

In order to load the chemical reagents into the ball in a premixed state so that they mix only when the ball is hit by an external force at the initial moment of use, the light-emitting ball is made as a container separated into isolated sections by easily breakable partitions so that separate reagents are loaded into separate isolated sections of the light-emitting body.

Depending on the method of inserting the containers of the light emitting body into a ball, the containers may have different shapes, as shown in Figs. 1 (a) through (d).

Fig. 1(a) is a transverse cross-section of a container having a cylindrical shape with partitions 11 and 12 that extend in the longitudinal direction of the container and that divide the container into separated segments that are filled with individual reagents A, B, and C. Figs. 1(b) and (c) are longitudinal cross-sections showing that the container may have a cylindrical, rectangular, or ribbon-like shape and that the interior of the container is divided into the aforementioned small cylindrical, rectangular, or ribbon-like sections by separating membranes 14, 15, and 16. The separated sections are filled with reagents A, B, and C, respectively. Fig. 1 (d) is a longitudinal sectional view of a cylindrical, rectangular, or ribbon-like container. Membranes 17, 18, and 19 divide the container into small spherical or ribbon-like sections which are filled with reagents A and B.

The shapes of the containers are not limited to cylindrical, rectangular, or ribbon-like and may be spherical, button-shaped, etc. They also may have different cross-sections, e.g., elliptical, rectangular, square, or round.

The separating membranes of the container should possess the strength that prevents breaking of the membranes under the effect of vibrations that occur during transportation but ensures breaking of the membranes under the effect of an external force with which the ball is stricken at the initial moment of use. Actual strength of the separating partitions will be chosen depending on the type of the ball filled with the light-emitting body, i.e., on the magnitude of a force that has to be applied to the ball during the game. The separating partitions can be made from glass, or the like, and the strength of the separating membranes can be adjusted by changing the membrane thickness.

The container can be made from a material capable of efficiently transferring an external force through the container to the chemical light-emitting composition. Such a material may be comprised of a transparent or light-permeable synthetic resin.

The amount of the aforementioned reagents that fill the container can be selected with reference to the time during which the ball is planned to be used in the games, but the optimal time for use of the ball is within 5 to 10 hours.

The chemical light-emitting composition that fills the container emits light when an external force is applied to the ball at the initial moment of use, the separation membranes are broken, and the reagents are mixed. After the separation membranes are broken, mixing of the reagents progresses because of movements or vibrations of the ball, so that during subsequent use of the ball,

emission of light continues.

The following description relates to a method used for inserting a light-emitting body in the form of a container filled with the chemical light-emitting composition into a ball.

A conventional ball may have a certain shape, e.g., the substantially spherical shape shown in Figs. 2(a) through (c). In the example of Fig. 2(a) that shows a filled-type ball, the latter consists of a core portion 21 which is coated with an outer shell 22. Such a ball may represent a golf ball, gate ball, hard football, softball, etc. Fig. 2(b) illustrates a ball that consists of a sealed air-filled inner part 23 and an outer shell 24. Such a ball is an example of a volley-ball, tennisball, or the like. Fig. 3(c) illustrates a single-component ball that consists only of an air-filled outer shell 25. The ball of this type is used as a soft tennis ball, soft football, etc. Such a ball is normally made from a natural or synthetic leather, fiber, rubber, or synthetic resin.

Figs. 3(a) through (g) illustrate methods to be used for inserting a container filled with the chemical light-emitting composition into a ball of the type shown in Fig. 2(a), i.e., a ball that consists of a core and an outer shell. More specifically, according to the method shown in Fig. 3(a), a cylindrical or ribbon-like lightemitting body 31 is wound onto the equator of the sphere inside the material of the shell 22. In the method illustrated by Fig. 3(b), light-emitting bodies 31, 32 are embedded into the outer shell 22 so that they are in contact with the surface of the core 21. In the method illustrated by Fig. 3(c), light-emitting bodies are arranged circumferentially over the interface between the core 21 and the outer shell 22 so that they are equally immersed into both members. In the method of Fig. 3(d), light-emitting bodies 32 are arranged circumferentially and are inserted into the core 21 but are maintained in contact with the outer shell 22. Fig. 3(e) illustrates an embodiment where ribbon-like, cylindrical, or button-like lightemitting bodies 33 are attached to the outer surface of the ball. Fig. 3(f) illustrates an embodiment wherein a light-emitting body 34 passes through the core 21 in a diametrical direction, and Fig. 3(g) illustrates an embodiment wherein a spherical light body 35 is arranged in the center of the core 21 and is provided with a plurality of optical fibers 36 that extend therefrom in a radial outward direction. In the specific examples of Figs. 3 (a) through (d), (f), and (g) the outer shells are made from a transparent or a light-permeable material, such as natural rubber, synthetic rubber, or synthetic resin.

Among the embodiments shown in Figs. 3(a) through (g), the embodiment of Fig. 3(f) has the most stable and simple construction with a high light-emitting effect, while the construction shown in Fig. 3(g) is advantageous because of a plurality of radially arranged optical fibers 36, thereby producing a great amount of light-emitting points.

A ball of the type shown in Fig. 2(b) that consists of an inner part 23 and the outer shell 24 can be equipped with light-emitting bodies by methods illustrated in Figs. 3(a) through (e) (i.e., either by inserting the light-emitting bodies into the inner part 23 or outer shell 24, or by placing them in the interface between the inner part 23 and outer shell 24; the light-emitting bodies may also be attached to the inner surface of the inner part 23 or to the outer periphery of the ball).

The ball of the type shown in Fig. 29(c) that consists only of a single outer shell can be equipped with light-emitting bodies, as shown in Figs. 3(a) or 3(e), i.e., either by embedding the light-emitting bodies into the material of the outer shell 25, attaching them to the outer surface of the ball, or attaching the bodies to the inner surface of the shell 25.

The light-emitting effect is increased when a luminescent agent is blended with the material from which the outer shell is made.

[Description of Practical Example]

The invention will be further described in more detail with reference to practical examples which should not be construed as limiting the present invention.

Practical Example 1 (Example of a Golf Ball)

A 5 ml solution was prepared from 1 mg of 9,10-diphenyl antracene in 1,2-dimethoxyethane (grime), 0.25 ml of water, and 0.5 ml of a 90% aqueous hydrogen peroxide; 3 mg of a bistriphenylacetic acid and oxalic acid anhydride were also prepared for the process. The first reagent was loaded into the section A of the cylindrical container shown in Fig. 1(b), while the second reagent was loaded into the section B of the same light-emitting body (reference numeral 14 designates a separating membrane made from glass). A ribbon-shaped light-emitting body and a button-shaped light-emitting body were also prepared from the same compositions.

Cylinder-shaped body: inner diameter in cross section - 6 mm

Ribbon-shaped body:

square cross-section – 3 mm x 3 mm rectangular cross-section – 3 mm x 1 mm elliptical cross-section – long diameter 3 mm; short diameter 1mm

Button-shaped body:

Cylindrical – diam. 10 mm, thickness 1 mm Rectangular - 10 mm x 5 mm, thickness 1 mm Elliptical – long diameter 10 mm, short diameter 5 mm, thickness 1 mm

All above-described light-emitting bodies were inserted into golf balls of the types shown in Figs. 3(b) through (d). Outer shells of the bodies were made from a transparent ionomer resin and were permeable to the light induced by the chemical reactions inside the bodies.

When the aforementioned golf balls were stricken by a golf club (#1W), the separating partitions inside the containers were broken, the chemical light-emitting reagents were mixed, and light was induced. Positions of the balls could be identified at a distance of 100 m ahead, and the balls were clearly visible even in dark places. This feature made it possible to accelerate the progress of the game, and since the flight direction of the ball could be observed, the game proceeded very smoothly and without accidents.

[Effects of the Invention]

As follows from the detailed description given above, the light-emitting ball of the present invention illuminates during a game and allows the games to proceed even under conditions of poor vision . Therefore, the game proceeds very smoothly, without accidents, and positions of the ball can be identified at any time. The principle of the invention is applicable to playing balls of various types. One indispensable condition for illumination of the ball is simply initiation of the game; the ball does not need any special means for switching on the light. The light-emitting ball of the invention is simple in construction and does not involve an essential increase in the production cost.

4. Brief Description of the Invention

Figs. 1 (a) through (d) are sectional views of containers for holding chemical light-emitting reagents. Figs. 2(a) through (c) are cross sections of conventional balls. Figs. 3(a) through (g) are cross sections that illustrate methods used for incorporating of light-emitting bodies with chemical light-emitting reagents into the balls shown in Fig. 2(a).

11 through 19 – separating diaphragms; 21 – core; 22, 24, 25 – outer shells



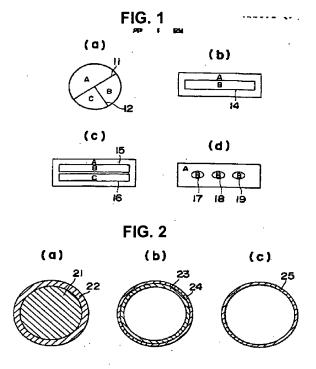


FIG. 3

